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Beg, M.M.

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A. E. K. Risø

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Abstract

Large single crystals of lithium-7 have been grown by the Bridgman method. Crystals were grown in sealed stainless steel thin walled containers, which could be used directly for the inelastic neutron scattering lattice dynamics experiments. The mosaic spread of the crystals varied between 25' and 45'.

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Growing Single Crystals of Lithium

M.M. Beg*

D.A.E.C. RISØ, DK-4000 Roskilde, Denmark.

(*Guest Scientiest from Pakistan Atomic Energy Commission)

1. INTRODUCTION

Large single crystals of lithium-7 have been grown by the Bridgman Method. The crystals were required to study the lattice dynamics of this metal by the method of coherent inelastic scattering of neutrons. Previously Bowers, Pinnow and Tallman[1] have grown crystals of lithium by the Czochralski method. The crystals grown by them had ½ cm diameter and were 3 to 6 cm long. As reported by Smith et al.[2] good single crystals of lithium-7 in suitably larger sizes for neutron lattice dynamics experiments were not available commercially. The main reason for the nonavailability of such crystals is the toxic and reactive properties of lithium which make handling of the material somewhat difficult.

Some of the physical and chemical properties of the metal which have to be kept in mind during a crystal growing project are given below. Natural lithium is a mixture of the Li^6 and Li^7 isotopes with the total atomic weight 6.94. Li^6 has a large neutron absorption ($\sigma(n,\alpha)$ = 1000 bn at 0.025 eV) and the isotope 7 is more useful for the neutron scattering experiments, although it gives large incoherent scattering (σ_{coh} = 0.8 bn; σ_{inc} = 1.2 bn). Lithium has a low density (= 0.53 gm/cc) therefore for a reasonable count rate in the neutron lattice dynamics experiments, crystals with diameter ∿ 1 inch are required. Other important physical quantities for lithium are melting point = 179° C; Boiling point = 1317° C; Heat of fusion = 179 cal/gm; Vapour pressure at 727° C = 0.78 mm; Thermal conductivity at 216° C = 0.11 cal/sec cm^3 ° C; Specific heat at 100° C = 0.9 cal/gm ° C; Coefficient of thermal expansion at 300 K = $47{*}10^{-6}$/° K. Lithium has a b.c.c. structure above 78 K with a lattice constant = 3.51 Å.

Lithium is chemically very reactive and unlike other alkali metals it reacts with nitrogen in the air forming LiN_3 which is black in colour and has a high melting point. Lithium metal is soluble in liquid ammonia and slightly soluble in ethylamine. It is insoluble in mineral oils. The reaction of lithium with water is very vigorous. The metal does not react with the noble gases argon and helium. Lithium reacts with ceramics, glass and quartz glass near its melting point. It has been reported to react with aluminum and most other metals(3) at high temperatures. In the presence of chlorides lithium attacks nickel in stainless steel, though lithium chloride free metal can be kept in stainless steel up to 450° C for few days. At higher temperatures in contact with lithium, steel is rapidly decarbonized. Pure iron equipment has been found safe to handle molten lithium up to 900° C. Lithium nitride frequently formed on the surface of lithium metal is a very reactive

compound. No metal or ceramic material has been found to be resistant to the molten nitride.

Lithium should be handled in a completely moisture, oxygen and nitrogen free argon or helium atmosphere. Lithium fire can be extinguished with graphite powder and chrome leather is the only protective clothing. Some of the useful references for handling lithium are[3,4 and 5]. LiO_2 a white, powder-like material formed on the surface of the metal is toxic and extremely irritating to the respiratory system.

2. CRYSTAL GROWING

The material available to us was 99.995 Li^7. The ingot was 1.125" in diameter and 2.75" long, weighing about 23 gm. Due to the shortage of material it was not possible to use the Czochralski method. The metal was transferred and sealed in specially designed thin walled stainless steel containers for crystal growing. The same containers were later used as samples for the neutron scattering measurements. The crystals were grown by the Bridgman method.

2a. Sample Containers

Fig. 1 shows the design of the containers used for crystal growing. The main body of the containers was 6 cm long with the inside diameter of either 1.2 cm or 2.2 cm. The lower part of the containers had a conical shape with a vertex angle of 75° and 90° for the containers with inner diameter 1.2 cm and 2.2 cm, respectively. The lower part of the cone terminated in a 1.2 mm wide and 12 mm long capillary tube, which in turn was joined to a 4 mm x 4 mm cavity at the bottom. The small cavity was provided to allow a uniform filling of the capillary. Any insoluble heavy impurities like LiN_3 in the form of fine particles could also settle down in the cavity instead of filling the capillary. It was found that containers with a cavity at the bottom gave better crystals. The upper part of the container was designed so that it could be sealed vacuum tight with the help of a soft iron seal using eight screws.

The walls of the container were machined to a thickness of 0.5 mm, so that the sample could be used directly for the neutron scattering experiments.

Before filling the sample container, the lithium was melted and filtered through a stainless steel wire mesh in an inert atmosphere.

2b. Filtration and the Sample Container Filling Procedure

Fig. 2 shows the schematic drawing of the lithium filtration and container filling system. Lithium metal was cut into small pieces, in a petsolium dish, using a glove box filled with helium. The surface of the metal was pealed off to remove the top nitride layer and the pieces were washed in benzene. The material was then transformed to a stainless steel filtration tube "B". The sample container "A" and the filtration tube "B" and the vacuum tubing up to the joint "C" were assembled in the glove box. The assembly "A" "B" "C" was joined to the vacuum and helium system such that the parts "A" and "B" were vertical. The system was evacuated to 10^{-5} mm of Hg and then filled with helium. The process was repeated several times to eliminate all traces of nitrogen. The tube "B" was

heated slowly with a gas flame and the metal filtered down to the sample container under gravity and helium pressure. The assembly "A", "B" and "C" was again transferred to the glove box where the container "A" was separated and sealed. The top 1 cm of the container was kept empty to allow for the volume expansion of lithium during crystal growing.

2c. Crystal Growing Details

The apparatus described by J. Als-Nielsen and W. Kofoed[6)] was used for growing the crystal. Fig. 3 shows a cross section of the crystal growing vacuum furnace. Lithium is contained in the container (1) described earlier, which is mounted in a holder (2). The holder is fixed on a stainless steel pedestal (4) through which heat conducts to the water cooled shaft (5). The shaft is led out of the vacuum through bearing (6) and is constantly rotated (4 rpm) by the motor drive (7) during the vertical translation furnished by the spindle drive (8). The gear wheels (9) are easily interchangable and a large number of velocities from 0.12 mm/h to 45 mm/h are readily obtainable. A perspex rod (10) connected to the shaft (5) indicates the position of the holder (2). The lower part of the lithium container is embedded in graphite which provides a good heat connection to the pedestal (4).

The system can be evacuated by means of a diffusion pump-rotary pump system. For growing lithium crystals we maintained a 0.2 atmosphere helium gas pressure in the furnace.

The heater (11) is connected to the top of the water cooled jacket (12) and these can be lifted as a unit. Between the heater and the outer jacket there are three irradiation shields of Mo foil. The furnace heater was modified by Allan Thuesen so that there is only one heater coil extended up to mark H. A copper pipe replaces the lower part of the heater shown in ref.[6]. The heater draws a current of 12 Amps. at 220 Volts. During the present work only 50-55 Volts were applied to the heater. Three thermocouples attached to the bottom, middle and top parts of the lithium container were used to monitor the temperatures. The maximum temperature at the top was kept below 320° C while the lower part of the container was at about 220° C. The system was kept at these conditions for about two days to obtain a uniform melting. Lithium has a high specific heat and a high heat of fusion and slow heating was found to be necessary. The crystals were grown in a vertical temperature gradient of 15-20° C/cm. The lowering speed through the gradient was 1.94 mm/hour and 2.4 mm/hour for the 2.2 cm dia and 1.2 cm dia crystals, respectively. If the speed was increased, a large number of grains were formed mainly due to increased horizontal temperature gradients in the melt.

Successfull attempts were made to grow both the natural lithium and Li^7 crystals. Single crystals obtained by the above procedure were of a reasonably good quality with a mosaic spread of $\sim$ 0.5 degree. But a few small grains were always present. In most cases the grains were small and did not affect the phonon

measurements. If it was found necessary to melt the crystal, the sealed container was put again in the ctystal growing furnace.

We did not take the crystals out of the steel containers and could not remove the small grains, which would have been possible if the Czochralski technique had been used. We could not use the Czochralski method due to the small quantity of material available to us and the lack of facilities to handle the alkali metal. However, we were able to get a good 5 cm long and 2.2 cm dia crystal of Li^7 in two attempts, with a mosaic spread of 0.5 degrees. This crystal had a small grain oriented at an angle of 27½ degrees with respect to the main crystal, which gave about 100 times smaller elastic scattering than the main crystal. This grain did not interfere much with the phonon measurements. A good quality 1.2 cm dia Li^7 crystal was also obtained in four attempts.

It may be noted that the crystal growing was not taken as a project itself. It would have been possible to refine the technique further if more material and time was available.

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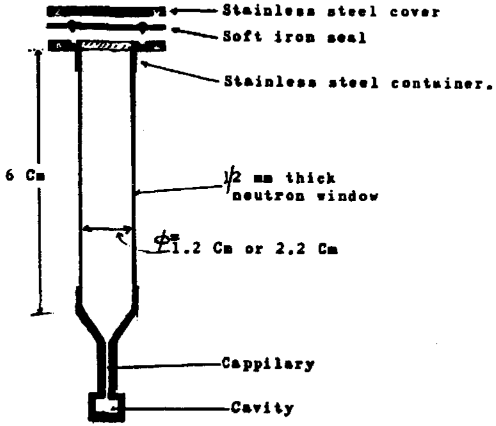

Fig 1:Li sample container for crystal growing and neutron scattering.

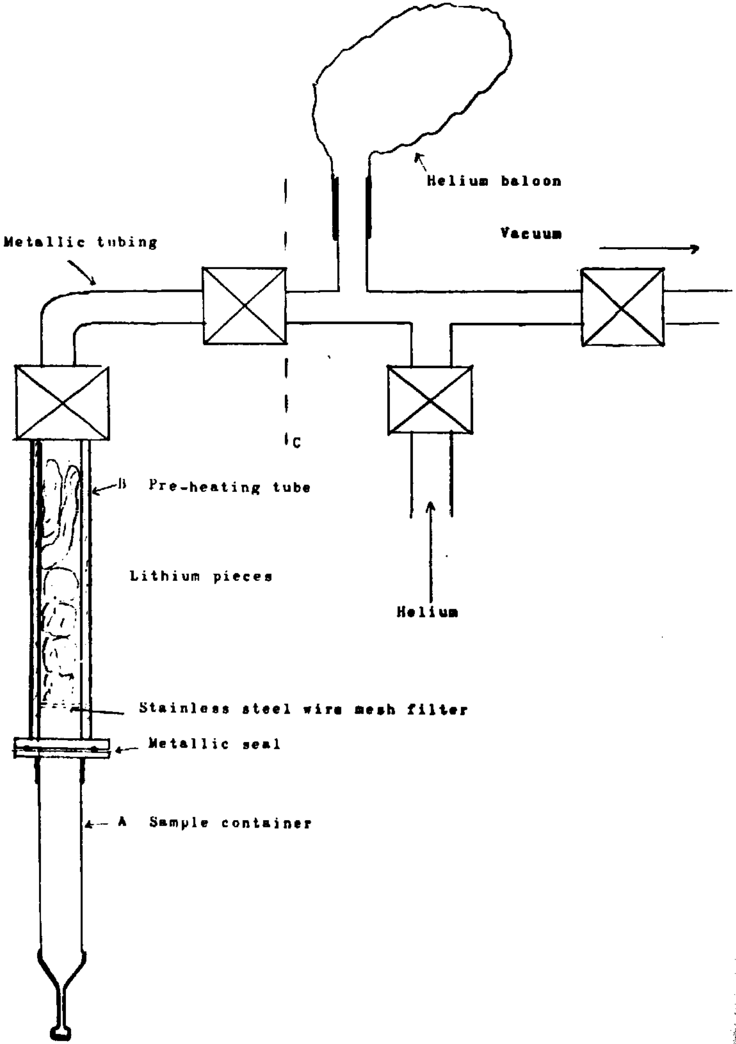

Fig 2 : Schametic diagram of sample filling and pre-heating system.